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(54) NITRIC ACID PULPING PROCESS

(71) We, KILBORN ENGINEERING LTD., whose post office address is 36 Park Lawn Road, Toronto 18, Ontario, Canada, a company organized under the laws of Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of pulp from cellulosic materials, for example wood, straws, grasses, fibrous vegetable material, bagasse, abaca and the like.

The use of nitric acid in pulping operations of cellulosic materials has traditionally been avoided, despite the fact that nitric acid is well known to react chemically with and remove lignins present in such materials. This is because nitric acid attacks cellulose as well as lignin, thereby deteriorating the quality of the resulting pulp.

Recently there has been proposed a pulping process which involves pre-impregnation of cellulosic material, in comminuted form, with nitric acid in the presence of ammonium hydroxide. The comminuted material is either impregnated with a mixture of nitric acid and ammonium hydroxide and then heated to initiate reaction of the acid with the lignins or the material is impregnated firstly with ammonium hydroxide and then with nitric acid, and then heated. Such treatment causes breakdown and/or oxidation of the non-cellulosic constituents of the material. After removal of the reactant liquor the material is washed and cooked with, for example, sodium hydroxide to complete the pulping. This process is claimed to enable conversion of the material to pulp to be carried out in shorter time, and under milder conditions of temperature, pressure and the amounts of reactants handled and consumed are less, thus reducing the expense thereof. In addition, the process enables pulp of a high quality to be produced, in higher yields, than with normal pulping processes.

The present invention provides a process of pulping non-pulped cellulosic reject material obtained from a previous pulping operation carried out on a cellulosic material which comprises impregnating the non-pulped cellulosic reject material with nitric acid in the presence of a non-basic ammonium ion-releasing compound, heating the impregnated material, separating the material from the excess impregnating liquor, washing the impregnated material, cooking the impregnated material with aqueous alkali, and recovering the pulp so formed. The use of the non-basic ammonium compound enables ready control of the process, to give high quality pulp in high yield.

The use of non-pulp rejects as at least a part of the cellulosic materials fed to this process, enables a pulp of superior quality to be produced. Moreover, the process can be repeated on the rejects until a very high yield of pulp, based on starting wood is achieved.

The preferred ammonium compound is ammonium nitrate, and the invention will be hereinafter described with reference to the use of ammonium nitrate.

The process of the present invention may be conducted as part of a multiple stage process, in which the first stage is conducted on a raw cellulosic material such as wood, and the second stage, which is in accordance with the present invention, is a repeat of the first stage but uses the rejects from the first stage, alone or in admixture with new wood or other cellulosic material. Then the conditions of the first stage are adjusted, not necessarily to obtain the minimum yield of rejects, but to obtain the

correct proportion of pulp and rejects to allow high quality pulp to be produced from the rejects after the second stage, and at an economically satisfactory rate. If desired, the process may have three or more stages, each involving reprocessing of the rejects of the previous stage alone or together with new material. The use of the multistage process according to this invention enables production of a high quality pulp, with comparatively high yields, and, if desired, practically complete utilization of the cellulosic starting material. The use of a multistage process enables higher yields of pulp to be produced, since the hemi-celluloses are retained to a greater extent in the pulp produced, than in conventional pulping processes.

In the process of the present invention, the impregnation of the material may be carried out in one or two steps. The material may be impregnated with a solution comprising a mixture of aqueous nitric acid and ammonium nitrate, or the material may first be impregnated with ammonium nitrate solution, and then with nitric acid. In either case, the comminuted material may first be steamed to facilitate impregnation. The impregnation time and conditions depend largely upon the nature and particle sizes of the material. The impregnation may take place at a temperature of from 0°C to 60°C, and most suitably from 20 - 50°C.

When the impregnation takes place in one step, the reactant (impregnant) liquor is preferably prepared from nitric acid aqueous solution having an acid concentration of from 3 to 22% by weight and preferably 15% by weight. To this nitric acid solution is added ammonium nitrate in an amount of 1 to 5 grams per litre of acid, and preferably in an amount of 2½ grams per litre. Impregnation takes place suitably for a period of one to ninety minutes, preferably 60 minutes, depending upon the method of impregnation. Then the excess liquor is poured off.

When the impregnation takes place in two steps, the material is first impregated with a dilute aqueous solution of ammonium nitrate. A solution containing from 1% to 10% by weight of ammonium nitrate is suitable with from 1% to 5% by weight being preferred. The impregnation suitably takes place for a period of from 30 to 60 minutes. Then the excess ammonium nitrate solution is removed, e.g. by pressing the material and decanting off the liquid. The next step is impregnation of the material with dilute nitric acid. The acid solution preferably has a density of 5° to 40° Baumé. The material is held in contact with the acid for some 30 to 60 minutes depending on particle size to impregnate it with the acid. Either or both impregnation steps can take place at atmospheric pressure, or at elevated pressures, e.g. up to 3,000 psi. Increasing the pressure reduces the time necessary for impregnation. After impregnation, the excess liquor is poured off.

The impregnated material is then heated to a temperature not exceeding 105°C and preferably from 75 to 97°C to initiate reaction of the nitric acid with the lignins. The material is held at this temperature for a period of from 15 to 75 minutes, to complete the oxidation reaction, whereupon the material is washed and otherwise chemically treated to free it from the nitric acid residue.

The cellulosic reject material is then cooked with an aqueous alkali to complete its conversion to pulp. Sodium potassium and ammonium hydroxides, in the form of 1 - 15% by weight aqueous solutions, are most suitable. The cooking time is from 5 minutes to 120 minutes, preferably from 30 to 60 minutes, at atmospheric or slightly elevated pressure. Then the material is again washed, and the pulped product separated from the non-pulped rejects, in a conventional manner. The entire process may then be repeated on the rejects, in accordance with the multistage process of the invention optionally mixed with fresh cellulosic material. The relative proportion of rejects to pulp produced in a single stage of the process can be adjusted by adjusting concentration of the nitric acid impregnant solution. The lower the acid concentration the lower the amount of pulp produced. Thus the yield of pulp can be adjusted to between 20% and 90% as desired. Normally the multi-stage process operated on wood chips can be adjusted to give 57 - 60% yield based on starting material. This is to be compared with a maximum 48% yield obtainable under comparable conditions using other nitric acid pulping processes.

The use of ammonium nitrate in the process shows considerable practical advantages over the use of ammonium hydroxide. Being an alkaline substance, ammonium hydroxide will react with, and hence consume nitric acid. Thus, in the two step impregnation process using ammonium hydroxide, the material, in the first stage, will absorb and retain some ammonium hydroxide, which will react with some of the nitric acid used in the second stage, reducing the amount of acid available for reaction with the lignins. Close control over acid concentration is desirable and indeed essential to enable one to obtain pulp of optimum quality, as indicated by the beater strength, brightness and lignin content of pulp.

With ammonium nitrate, however, this problem is overcome. The nitrate is non-

reactive with the acid and so does not reduce the amount of acid available for reaction. Hence the actual amount of nitrate retained by the material after the first step of impregnation is of no consequence. Close control over nitric acid amounts is therefore possible.

Similar advantages are derived in the one step impregnation process. The ammonium nitrate and nitric acid are non-reactive towards one another, and so no special allowances or precautions have to be adopted in preparing the reactant liquor. This avoids waste of nitric acid. In addition, ammonium nitrate is a much more convenient material to handle than ammonium hydroxide, being stable in solution, non-volatile, non-noxious and not subject to loss of strength on standing.

The economics of the process of the invention may be further enhanced by recovery of the gases generated during heating of the pre-impregnated product. These largely comprise a mixture of nitrogen oxides. The mixture can be readily oxidized to nitrogen dioxide, for regeneration of nitric acid. Alternatively, the nitrous oxide can be isolated for its other well known uses in the medical field.

The process of the invention does not give rise to problems commonly encountered in nitric acid pulping, which is that nitric acid tends to attack the cellulose, and lead to the formation of brittle fibres. The presence of the ammonium ion appears in some way to modify the action of the nitric acid, and a high quality pulp is readily and economically obtained from a process utilizing this invention.

The process of the invention is also useful in conjunction with conventional pulping processes. Thus the non-pulped rejects emanating from a conventional pulping process may be treated by impregnation with nitric acid and ammonium ions, heated, washed and cooked with sodium hydroxide solution in accordance with the invention, to produce pulp with desirable properties. The rejects may emanate from a process using bisulphites or from a process using sulphates and sulphides along with caustic solutions, or any other conventional pulping process.

The invention will be further described with reference to the following specific example. Test data were determined by standard TAPPI procedures.

A sample of southern pine rejects from a previous pulping operation was impregnated with 13.3% by weight nitric acid containing 4.7% by weight ammonium nitrate at room temperature for 1 hour in a closed vessel. Six successive evacuations with intermediate acid submersion at atmosperic pressures were undertaken. Excess acid was drained off and steaming was done for 30 minutes at 100°C. After washing, the chips were treated with 1.1% by weight ammonium hydroxide solution at 100°C for one hour.

A yield of 65.6% pulp based on dry wood was obtained along with 5.4% rejects. In the pre-impregnation the wood consumed 21.2% of its own weight of nitric acid. In the pulping operation 5.3% of ammonia based on the weight of the wood was consumed.

The resulting pulp had a Kappa number of 12.0 ml and a viscosity of 13.9 cp.

WHAT WE CLAIM IS:—

1. A process of pulping non-pulped cellulosic reject material obtained from a previous pulping operation carried out on a cellulosic material which comprises impregnating the non-pulped cellulosic reject material with nitric acid in the presence of a non-basic ammonium ion-releasing compound, heating the impregnated material, separating the material from the excess impregnating liquor, washing the impregnated material, cooking the impregnated material with aqueous alkali, and recovering the pulp so formed.

2. The process claimed in claim 1 wherein said non-basic ammonium ion-releasing compound is ammonium nitrate.

3. The process claimed in either of claims 1 or 2 wherein the cellulosic reject material is impregnated with a nitric acid aqueous solution having a nitric acid concentration of from 3 to 22% by weight.

4. The process claimed in claim 3 wherein the said aqueous solution also contains from 1 to 5 grams of ammonium nitrate per litre of acid.

5. The process claimed in either of claims 1 or 2 wherein said cellulosic reject material is impregnated with an aqueous solution of 1% to 10% by weight of ammonium nitrate, excess ammonium nitrate solution is removed, and the material is then impregnated with an aqueous solution of nitric acid having a density of from 5° to 40° Baumé.

6. The process claimed in any of the preceding claims wherein the cellulosic reject material comprises non-pulped cellulosic reject material admixed with fresh cellulosic material.

7. The process claimed in any of the preceding claims wherein the impregnated material is heated to a temperature of from 75 to 97°C, so as to initiate reaction of the nitric acid with the lignins.

8. The process of claim 7 wherein the impregnated material is subsequently cooked with a 1 to 15% by weight aqueous solution of sodium, ammonium or potassium hydroxide.

9. A process of pulping non-pulped cellulosic reject material according to claim 1 and substantially as described herein with reference to the Example.

10. Pulped cellulosic pulp whenever prepared by a process claimed in any of the preceding claims.

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